

## Paramagnetic Behavior of Ni-Fe Layered Double Hydroxide and their effect over the Electrocatalytic Activity towards Oxygen Evolution Reaction in Alkaline Media

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### ABSTRACT

In the present work the hydrotalcite like materials know as Layered Double Hydroxide (LDH) Ni-Fe with different Ni/Fe relationship were synthesized by co-precipitation method to constant pH, the LDH obtained were labeled H/Ni-Fe1 and H/Ni-Fe2, the hexagonal lattices with R3m rhombohedral symmetry, characteristic for this materials was verify by XRD, No secondary phases are observed for any materials. On the other hand, the electronic properties were evaluated by Electronic Paramagnetic Resonance (EPR), the results suggested that H/Ni-Fe1 exhibited a ferromagnetic behavior as a result of the combined action of NiII-OH-NiII and FeIII-OH-NiII and FeIII-OH-FeIII pairs across the layers and ferromagnetic dipolar interactions operating between layers. Whereas, the H/Ni-Fe2 presented a Paramagnetic behavior due to intralayer magnetic superexchange between metal centers through the OH bridges across the cationic sheets and dipole-dipole interaction in sites of less distorted octahedral field which operating through the space between the magnetic layers. These materials were evaluated as electrocatalyst in the Oxygen Evolution Reaction (OER) in alkaline media, the results showed that OER begin c.a. to 1.4V/NHE, the tafel plots for both materials were around to 39mV dec<sup>-1</sup> which is comparable with IrO in same media. However, the Turn Over Number (TON) value was 9.9 s<sup>-1</sup> for H/Ni-Fe1 and 38.1 s<sup>-1</sup> for H/Ni-Fe2, indicating the higher electrocatalytic behavior in H/Ni-Fe2 than H/Ni-Fe1, this interesting result were discusses by electronic properties determinate in EPR experiments.

*Keywords:* LDH, Paramagnetic, Turn Over Number



## 1. Introduction

The electrolysis of water to produce hydrogen and oxygen gas (i.e., water splitting,  $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$ ) is a key component in the development of future energy storage technologies. The oxygen evolution reaction  $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$  (in basic media) is kinetically slow and hence represents a significant efficiency loss. The oxygen evolution mechanism has several steps that have large reaction barriers, which lead to large required overpotentials to drive the reaction at practical rates. The large overpotentials significantly decrease the efficiency, as the extra energy is dissipated as low quality heat, and limit the possibility of large scale production of hydrogen from water splitting. Therefore, considerable research efforts have been made in developing the OER electrocatalysts which are highly active, stable and inexpensive. The oxides of Ru and Ir are considered as the best OER catalysts for use in acid and base respectively, but these metals are amongst the rarest elements on the earth and, hence, are not economical for large-scale applications [1].

Nickel and its alloys have been traditionally the materials of choice for anodes in the process of alkaline electrolysis of water oxygen evolution reaction (OER), it has relatively low overpotentials, low cost, long-term stability and high corrosion resistance. Ni-Al and Ni-Fe LDH catalysts have been shown to be of particular interest because of the lower overpotential of reaction and the stable activity [2].

Layered double hydroxides (LDHs) are a group of inorganic materials that contain positive charged in the layers region. The composition of the main layer can be written as  $[\text{M(II)}_{1-x}\text{M'(III)}_x(\text{OH})_2]$ , with the positive charge on the main layer resulting from the replacement of divalent ions with trivalent ions. Both divalent and trivalent ions are located at the center of octahedral composed of  $\text{OH}^-$  ions;  $\text{M}(\text{OH})_6$  and  $\text{M}'(\text{OH})_6$  octahedral units share edges forming 2D layers. The interlayer incorporates anions and water molecules to maintain charge neutrality [3]. In this work we report the oxygen evolution reaction (OER) using hydrotalcite-like (LDH) materials

## 2. Experimental

The Ni-Al and Ni-Fe LDH were prepared by coprecipitation as described elsewhere. As an example, Ni-Fe<sub>2</sub> was prepared by dissolving 0.117 moles of NaOH (Aldrich) and 0.034 moles of  $\text{Na}_2\text{CO}_3$  (Aldrich) in 100 mL of deionized water; the pH of this solution was 13.4. A second solution was prepared by dissolving 0.034 moles of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich) and 0.017 moles of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Aldrich) in 100 mL of deionized water. While maintaining the first solution under vigorous stirring the second solution was slowly added by means of a peristaltic pump. After complete addition the resultant slurry was stirred for 2 h at room temperature; the pH of the suspension was 9.5. Finally, the suspension was stirred for 2 days at 50 °C, and then the solid obtained was separated by centrifugation, rinsed thoroughly with warm distilled water, and dried overnight at 80 °C. The solids obtained were labeled H/Ni-Fe1 and H/Ni-Fe2, where the number indicates Ni/Fe ratio.

The modified carbon paste electrode were prepared mixing graphite powder (Alfa Aesar, 99.9995%, USA), silicon oil (Aldrich) and the corresponding LDH at 20 wt.%. The mixture was mechanically homogenized and inserted in 2 mm diameter cylinder (0.0314 cm<sup>2</sup>). The surface contact on the electrode was made with a platinum wire.

The XRD structural characterization of LDHs was performed in a Philips X'PERTPRO instrument using  $\text{CuK}\alpha 1$  radiation ( $\lambda = 1.542 \text{ \AA}$ , 45 kV, and 40 mA); Electron Paramagnetic Resonance (EPR)



measurements were carried out at room temperature and 77 K using a JEOL JES-RES3X continuous wave EPR spectrometer. Typical EPR spectral parameters were as follow: X-band frequency = 9.1642 GHz, modulation amplitude = 3.2 G, modulation frequency = 100 kHz.

Electrochemical analyses were carried out at room temperature in a potentiostat–galvanostat VERSASTAT3-400 (Princeton Applied Research). A three-electrode standard electrochemical cell was used for the cyclic voltammetry (CV) measurements at  $5 \text{ mV s}^{-1}$  with a carbon rod and a Saturated Calomel Electrode (SCE), respectively. For these experiments, the working electrode was made from the synthesized materials, immersed in a carbon paste electrode (CPE) matrix.

### 3. Results and discussion

#### *Materials Characterization*

Lamellar structure of solids was confirmed by X-ray diffraction, infrared spectroscopy and Raman spectroscopy. The powder X-ray diffractograms of the synthesized samples are shown in Figure 1. All samples exhibited the typical signature of hexagonal lattices with R3m rhombohedral symmetry (JCPDS card 22-0700), any secondary phases were observed.

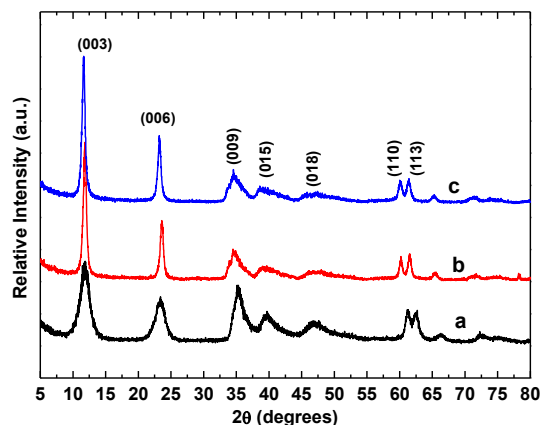


Figure 1. X-Ray Diffraction patterns of a) H/Ni-Al, b) H/Ni-Fe1 and c) H/Ni-Fe2

The H/Ni-Al EPR spectra exhibited a very broad and weak signal around  $g = 2.2014$  (Figure not shown), which has been attributed to the  $MS=0$  and  $MS=\pm 1$  magnetic dipole transition of NiII. This phenomenon is favored by orthogonality of the NiII magnetic orbitals due to NiII-OH-NiII interaction, where the angle in the LDH structure should be close to  $90^\circ$ . On the other hand, the H/Ni-Fe samples showed broad signals around  $g = 2.0248$  (Figure 2B) which are characteristic of FeIII low spin with  $S=1/2$ . The line width ( $\Gamma$ ) and the morphology of the EPR spectra indicate a strong FeIII-OH-FeIII interaction with an important



contribution of FeIII-OH-NiII interaction. However, due to the composition of LDH materials NiII-OH-NiII interaction could not be discarded.

Both samples presented interesting differences in the EPR spectra. The H/Ni-Fe2 sample shown a weak and broad signal at 300 K (Figure 2) but at 77 K this EPR signal was increased. This behavior suggests that the sample exhibits an antiferromagnetic (AF) interaction with a small contribution of ferromagnetic (F) interaction at 300 K. However, ferromagnetic interaction is increased at 77 K. This fact could be explained due to the Ni-Fe hydrotalcite like materials behave as ferrimagnets, as a result of the combined action of F NiII-OH-NiII and AF FeIII-OH-NiII and FeIII-OH-FeIII pairs across the layers and ferromagnetic dipolar interactions operating between layers.

On the other hand, H/Ni-Fe1 showed an intense EPR signal with line width  $\Gamma = 285$  Gauss and  $g = 2.2014$  at 300 K, which is characteristic of paramagnetic behavior (Figure 2B curve a). Furthermore, at 77 K the line width of the EPR signal was increased notoriously, indicating the presence of a ferromagnetic behavior among the Fe spins; however, the paramagnetic behavior shown at 300 K can still be seen at this temperature. The paramagnetic behavior of H/Ni-Fe1 could be associated to the increase of iron content. As a result of this increase may be that: 1) an increment in FeIII-OH-FeIII interactions, which generate a spin glass process in this material due to the spin frustration. In addition, these iron interactions could promote the intralayer superexchange interaction between metal centers through the OH bridges across the cationic sheets; 2) a dipole-dipole interaction in sites with distorted octahedral field, which operate through the space between the magnetic layers.

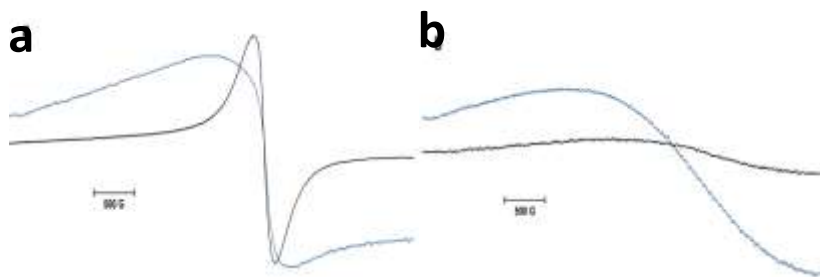


Figure 2. EPR spectra of a) H/Ni-Fe1 and b) H/Ni-Fe2, black line at room temperature and blue line at 77K.

#### *Electrochemical characterization*

The current-potential characteristics obtained in 1M KOH solution at  $5 \text{ mV s}^{-1}$  for LDHs immobilized in a Carbon Paste Electrode (CPE), are displayed in Figure 3. For H/Ni-Al (curve a) an anodic peak at ca. 1.52 V/RHE is observed and might be associated with the oxidation of NiII to NiIII, followed by the OER starting at ca. 1.6 V/RHE. Conversely, for H/Ni-Fe1 and H/Ni-Fe2 samples (curve b and c) the obtained



profiles indicated that only OER is carried out, starting at ca. 1.46 and 1.48 V/RHE, respectively. According to these results, the current magnitude order during oxygen evolution was as follow: H/Ni-Fe1>H/Ni-Fe2>H/Ni-Al.

On the other hand, the current-potential characteristic obtained using cyclic voltammetry (CV) for H/Ni-Al displays well-defined anodic and cathodic peaks associated with redox process for the couple NiIII/NiII with a peak-to-peak potential  $\Delta E_p=200$  mV, see inset in Figure 3. This electrochemical behavior is well-known and is due to insertion/desertion of OH<sup>-</sup> ions from the LDH-interlayer space during nickel-sites oxidation/reduction by electron hopping mechanism along the brucite structure inducing electro-neutrality. It is worth to mention that non-faradic processes were observed at CPE free of LDH (Figure not shown).

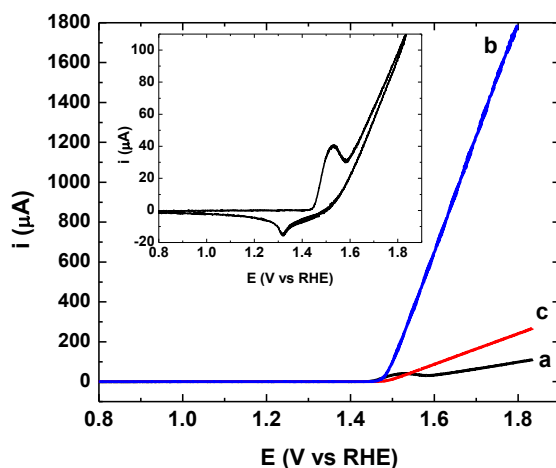


Figure 3. Linear Sweep Voltammetry of a) H/Ni-Al, b) H/Ni-Fe1 and c) H/Ni-Fe2, inset: cyclic voltammetry of H/Ni-Al in 1M KOH.



Tafel plots obtained from polarization curves were fashioned (Fig. 4). The resulting Tafel slopes were ca. 34, 36 and 37 mV dec<sup>-1</sup> for H/Ni-Al, H/Ni-Fe2 and H/Ni-Fe1, respectively. These values are smaller than those reported for the system Ir/C which exhibited a Tafel slope of ca. 40 mV dec<sup>-1</sup>; indicating that, within experimental error, the OER mechanism is similar for all set of these materials. Such reaction mechanism might be related with i) a surface oxidation by one electron electrochemical step; ii) adsorption step; and iii) a one electron-electrochemical rate-determining step for oxygen production.

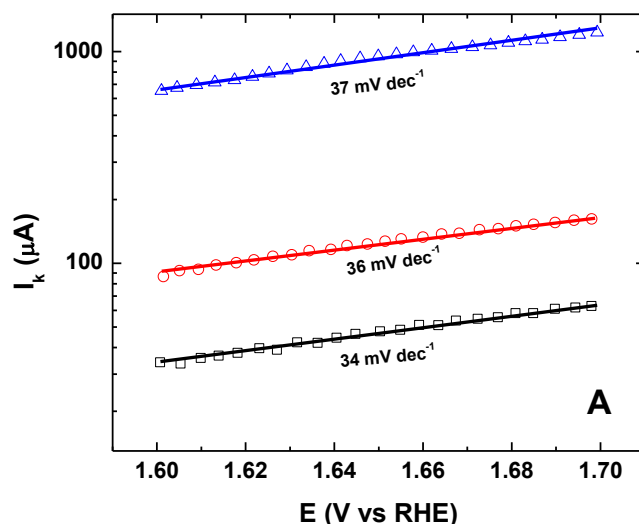


Figure 4. A) Tafel Plots of a) H/Ni-Al, b) H/Ni-Fe1 and c) H/Ni-Fe2 obtained from i-E characteristic of Fig. 3

#### 4. Summary and perspectives

LDH materials with different Ni/Fe ratio using co-precipitation method at variable pH were synthesized. The iron content in the structure of these materials plays an important role on their magnetic properties. It may be postulated that the superexchange interaction is one of the main causes that promotes the enhancement of the H/Ni-Fe1 catalytic activity toward OER. Production of molecular oxygen were confirmed using LSV. Whereas, Tafel slopes were around 40 mV dec<sup>-1</sup>, indicating that every materials rules out by the same mechanism reaction, where one electron electrochemical is the rate determining step for O<sub>2</sub> production.

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